

INTERACTIONS OF MOLECULES WITH LIPID-MODIFIED ELECTRODES AND CHEMICALLY INDUCED LIPID FILM DYNAMICS

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Interactions of various compounds with model lipid membranes supported on metal electrodes have been investigated with and without incorporating of ion-channel forming molecules. The interactions of drugs and biomolecules with lipid membranes is an important factor in their biological activity. Self-assembling layers of three types of phospholipids with different charge on the head groups have been examined: L- α phosphatidylcholine (PC), cardiolipin (CL), and phosphatidylethanolamine (PE). The electrochemical activity of a variety of compounds including neuroleptic drugs, sulfur compounds, neurotransmitters, antibiotics, and quinones have been tested. A considerable increase in anodic voltammetric peak height for oxidation of positively charged hydrophobic organic molecules was observed for CL films, in which the inner-most plane of the adsorbed head groups is negatively charged. Here, the hydrophobic interaction of organic cation with CL tails is enhanced by the strong electrostatic attraction between the cation and CL head groups, resulting in a deep penetration of the guest cation into the CL membrane. The operation of electrostatic forces in the environment of hydrophobic lipid tails is corroborated by a decrease in electrochemical activity of guest cations in PE films. In this case, the lipid heads bear the same charge as the guest molecule, which results in a reduction of the guest molecule penetration depth and a decrease in the electron tunneling probability. Using a sensitive Electrochemical Quartz Crystal Nanobalance (EQCN) technique, we have found that the guest dications formed in lipid film during oxidation are expelled from the lipid film despite of availability of counter-ions in high concentration in the solution. The lipid film, however, remains stable and is not desorbed from the electrode surface.

The chemically-induced dynamics of supported bilayer lipid films (BLM) was investigated by cleavage of the bonds BLM/substrate and build-up of a foreign interlayer between the BLM and the substrate. First, ion channels in a supported BLM were formed by incorporating

gramicidin (GR) molecules, which have a β -helix structure with wide internal channel and are permeable to Tl⁺ ions, as shown by Nelson [1]. The Quartz Crystal Immittance (QCI) measurements have shown that a DPPC_{BLM}/GR film on Au electrode is at room temperature in the solid state and behaves as a perfectly rigid film. The potential step chronopiezogravimetric experiments indicate that Tl atoms can be deposited at the interface Au/lipid film and form a Tl-UPD interlayer [2]. Sharp resonant frequency spikes, associated with Tl-UPD formation and dissolution, have been observed and explained by Tl-UPD induced lipid film lifting with intermediate lipid aggregation. Similar phenomenon of frequency spiking has also been observed in other systems, e.g. during a chronoamperometric reduction of thin metallo-organic salt films on Hg-EQCN electrode.

References

1. A. Nelson and D. Bizzotto, *Langmuir*, **15** (1999) 7031.
2. M. Hepel, *J. Electroanal. Chem.* (submitted).